

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP05/000354

International filing date: 14 January 2005 (14.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 04447013.6
Filing date: 16 January 2004 (16.01.2004)

Date of receipt at the International Bureau: 24 March 2005 (24.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in
compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Anmeldung Nr:
Application no.: 04447013.6
Demande no:

Anmeldetag:
Date of filing: 16.01.04
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Tomas Lewis BVBA
Kerklei 65
2960 Sint-Job-in't-Goor
BELGIQUE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Improved laminates

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B32B/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

Bemerkungen:
Remarks:
Remarques:

The application was transferred from the above mentioned original applicant to:
Domo Oudenaarde NV - Oudenaarde, Belgium
The registration of the changes has taken effect on 01.09.2004.

+3292802345

1

Improved laminates

Field of the invention

The present invention relates to laminates. In particular, it relates to a floor covering formed of laminated panels. More in particular it relates to floor laminate comprising
5 photocatalytic particles having many functions of antimicrobial, preventing smell or stainproof, or decomposition of harmful substances (NOx, and the like) based on the photocatalytic function.

Background of the invention

Decorative laminates are well known and used for instance as covering material on walls,
10 cupboard doors and desks, on tables and other furniture and as flooring material.

Such laminates are often made of a base of particle board or fiber board provided with a monochromatic or patterned decor sheet impregnated with melamine-formaldehyde resin and a fine so-called overlay sheet of a-cellulose impregnated with melamine-formaldehyde resin. These sheets can be laminated to the base under heat and pressure.
15 The individual laminate boards made from the laminate covered fiber board are usually furnished with some kind of tongue-groove joint in the side edges. The overlay sheet is intended to protect the decor sheet from abrasion. In certain cases the overlay sheet is omitted.

Since long the industry of laminated flooring tries to enhance the technical properties of
20 laminated flooring. In the past the main focus has been laid on the technical performance of the product such as better carrier boards, lower expansion coefficient, click system, better durability and abrasion resistance of the surface.

The decorative layer can be protected by either an overlay of paper saturated with melamine resins and a certain content of AlO_2 to make the product abrasive resistant, or
25 by saturation of the decorative printed paper with a suspension of melamine urea formaldehyde resins and a certain amount of aluminum oxide. Another method to treat and protect the decorative layer is the application of lacquers and hardening with electron beam curing.

However, although the floor covering produced nowadays have enhanced mechanical
30 properties, they still have several disadvantages such as for example the continuous release of harmful substances. Moreover, floor coverings are usually strongly glued by synthetic adhesives. Synthetic adhesive having fungus resistance performance are often

+3292802345

2

used. In addition, there are many cases where building residents complain of symptoms such as irritation of eye and nose, headache, tiredness and drying of throat and skin, as a result of the floor covering employed. The health hazard showing such symptoms is called a sick house syndrome and has become a social problem. It is considered that the main cause is solvents used for adjustment of synthetic adhesives, for example, formaldehyde (it is also a carcinogen) derived from formalin.

In addition, surface treatments are often used in order to protect the floor coverings and to polish them. As the surface treatment, synthetic resin, for example, acryl resin emulsified polishing agent and a product filled in a synthetic resin bottle with a nozzle for spray is generally used. However these polishing agents often contain solvents harmful for human body. In addition, living spaces of residences and offices may carry airborne malodorous substances including sulfur compounds such as hydrogen sulfide and methyl mercaptan, nitrogen compounds such as ammonia, and other compounds such as fatty acid. To provide a comfort of living environment, it is desirable to treat the contaminated air for removal of the malodorous substances.

It is an object of the present invention to provide an improved floor covering wherein the volatilization or release of organic solvents is reduced. It is another object of the present invention to provide an improved floor covering having fungus resistance and bacterial resistance properties. It is a further object of the present invention to provide a floor covering which is abrasion-resistant. It is yet a further object of the present invention to provide a floor covering having deodorizing and stainproofing properties.

Summary of the invention

In a first aspect, the present invention provides laminates comprising a decorative upper layer, optionally a protective overlay and optionally a base layer, wherein said decorative upper layer comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

The present invention also provides laminates comprising a decorative upper layer, a protective overlay and optionally a base layer, wherein said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

In a second aspect the present invention provides decorative layers for laminate comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

+3292802345

3

In a third aspect the present invention provides protective overlays, wherein said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

5 The present invention also provides a process for the production of a decorative layer or a protective overlay according to the present invention, comprising the step of providing a fiber web layer, treating said fiber web layer with a composition comprising photocatalyst particles, a binder and a solvent, and hardening said treated fiber web to obtain a decorative layer or a protective overlay comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

10 The present invention provides the advantage that the laminates, the decorative layer and the overlay according to the present invention are excellent in the points that they show a deodorant function, an antimicrobial function or an antistain function due to photocatalyst particles comprised in said laminates.

15 The laminates of the present invention have the advantages of being anti staining, selfcleaning, antimicrobial and desodorizing. The photocatalyst particles comprised in said laminates will actively decompose toxic and non-biodegradable pollutants. Said photocatalysts will also mineralize any organic pollutants into CO₂, H₂O and inorganic compounds. These reactions can be activated by the sunlight, and when said photocatalysts are tuned by visible light.

20 The object of the present invention is to provide a photocatalytic process for treating an indoor environment contaminated by bacteria and airborne particulate or volatile substances which may be carried out without resort to a light source which is harmful to human being.

25 The laminates, overlay, or decorative layers according to the invention do not necessitate the use of a special light source for excitation of the photocatalyst particles. They permit to photocatalytically treat an indoor environment or air. When bacteria and/or airborne substances are brought in contact with the photocatalyst particles comprised in said laminates, they are photodecomposed in situ.

Detailed description

30 The present invention relates in particular to laminates comprising a decorative upper layer, optionally a protective overlay and optionally a base layer, characterized in that the decorative upper layer comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder. In another embodiment, the laminates

+3292802345

4

according to the invention comprise a decorative upper layer, a protective overlay and optionally a base layer, characterized in that said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

- 5 The term "a protective overlay" as used herein refers to one or more overlay.

The term particle is to be understood in a very broad sense, including powders, dusts, fine granulates, fillings and fibers, i.e. all forms of particles able to be distributed over a surface in a largely even manner.

- 10 The overlay and the decorative layer according to the present invention comprise a fiber web made of any suitable fiber. In an embodiment of the present invention said fibers are cellulose fibers. However, other materials, either on the basis of cellulose or not, are not excluded. Preferably said overlay and the decorative layer are made of thin sheet of paper.

- 15 As an example of the photocatalyst particles, which may be deposited into and/or onto these laminates, overlays or decorative papers, there may be mentioned oxide and non-oxide semiconductors such as TiO_2 , ZnO , SiO_3 , $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, SrTiO_3 , Fe_2O_3 , CdS , CdSe , WO_3 , FeTiO_3 , GaP , GaAs , GeAs , RuO_2 , MoS_3 , LaRhO_3 , CdFeO_3 , Bi_2O_3 , MoS_2 , In_2O_3 , CdO , SnO_2 , SiC , InP and/or mixture thereof. In a preferred embodiment TiO_2 , ZnO , SiO_3 , CdS , CdSe , GaP , MoS_3 , SiC , and the like are used. In an embodiment they are used on a
20 nanoscale size. They are excellent in the points that they show a deodorant function, an antimicrobial function or an antistain function due to decomposition of an organic compound by oxidation. Among these, TiO_2 , Fe_2O_3 , ZnO , SnO_2 , and the like are available in the point that starting materials are obtained cheaply, and further an anatase type TiO_2 and SnO_2 are more preferred in the point that fine particles having higher activity can be
25 easily obtained. Rutile form TiO_2 metalized with copper, silver, platinum or other metals may also be used. The photocatalyst particles having photocatalytic function of the present application may be used either any one kind of these or in combination of two kinds or more by mixing.

- 30 Photocatalyst described herein are able to break down many organic pollutants totally or partially. In an embodiment of the present invention, TiO_2 as anatase is preferred since high photocatalytic purification has been observed because of its strong oxidation power, high chemical durability and non-toxicity. TiO_2 is an inorganic oxide, showing no absorption of any fraction of the visible light, thus it is not colored. In the region of shorter wavelength a strong absorption of UV radiation is observed. This is due to the promotion

+3292802345

5

of an electron out of the valence band into the conductive band. In its anatase modification the band gap is 3.05 eV. In its tuned form the band gap is 2.8 eV. In this process photo energy is transferred into chemical energy.

Without being bound by the theory it is believed that active oxygen species generated from the laminate according to the invention, act on a bad smell component or bacteria to show a deodorizing property or an antimicrobial property, and the like.

In an embodiment of the present invention, said photocatalyst particles may be doped or tuned by adding one or more element within the crystal lattice of said photocatalyst. In an embodiment of the present invention, said photocatalyst particles can be doped with elements selected from the group comprising Nb, Mo, Cr, V, Cu, Mg, Ag, Ru, Au, N, Nd, Pd, Pt, Fe, Ni, Mn and the like. Said elements can be the atom as such or ion form of said atoms. They can be implanted from the surface to deep inside of the bulk of the photocatalyst in an amount of at least 10^{15} ions per g of the photocatalyst. For example, incorporating specific metal ions into the titanium oxide catalysts allows the catalyst to absorb light not only in the ultraviolet region but also in the visible light regions of about 400 to 800 nm.

The present invention provides laminates comprising overlay layer or decorative layer having a web of fiber comprising photocatalyst particles embedded in a suitable binder. Non-limiting examples of suitable binder include melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamide resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof.

The binders for use according to the invention may be modified so as to impart a hydrophobe and/or oleophobe surface properties to the laminate.

In another embodiment of the present invention, the laminate may comprises a decorative layer as used in the prior art and an overlay according to the invention. Said decorative layer for example, can be made of paper impregnated with resin, which can be imprinted with a variety of patterns, such as a wood pattern, a pattern in the form of stone, cork, or similar or even with a fancy pattern.

It is clear that still other layers can be provided to the laminate, such as an intermediate layer upon which the decorative layer is provided.

+3292802345

6

The base layer of the laminate of the present invention may be selected from the group comprising of fiber board, particle board, a plastic sheet, wood and the like. Said base layer may be made of finely-ground wood which preferably is glued, more particularly, watertight glued. Still more particularly, said base can be made of HDF board (High Density Fiberboard) or MDF (Medium Density Fiberboard). In a preferred embodiment, said base layer is MDF.

Preferably, also a backing layer, also referred as balancing sheet or counteracting layer, can be applied at the underside of the base layer forming a counterbalancing element for the top layers and, thus, guaranteeing the stability of the form of the floor laminate. This balancing sheet may consist of a material, for example paper, impregnated with a resin, for example, a melamine resin.

It was surprisingly found that the laminates according to the invention exhibit anti staining, selfcleaning, antimicrobial and deodorizing properties. These laminates have a surface profile with improved properties over the current art.

The present invention further relates to decorative layers as described above. In a preferred embodiment, said decorative layer is made of cellulose fibers, such as paper. According to the present invention, said decorative layer is impregnated with a composition comprising photocatalyst particles and a binder. Examples of suitable photocatalysts have been described herein. Preferably said decorative layer comprises on or in its fiber web TiO_2 particles, and more preferably anatase TiO_2 . As previously cited the photocatalyst particles used in said decorative layer may be doped with elements as described above. Suitable binders embedding said particles are the same as that described above.

The decorative layers according to the invention according to the present invention can be used for manufacture and decoration of laminates, furniture components, flooring laminates and other surfaces where decoration is needed.

The present invention also relates to protective overlay comprised of a fiber web having deposited thereon or therein photocatalyst particles embedded in a binder. Suitable binders embedding said particles are the same as that described above. Suitable photocatalyst particles comprised in said overlay are the same as that described above. Said photocatalyst may be additionally doped as described above. In a preferred embodiment, said overlay is provided with TiO_2 particles and more in a particular with anatase TiO_2 .

+3292802345

7

In a preferred embodiment the protective overlay is made of one or more material layers such as cellulose fibers for example very thin layers of paper. Said overlay may be a transparent or translucent, specially made cellulose paper into which additional abrasion-resistant particles can be woven, or which can be impregnated with any other abrasion-resistant particles, which give the laminate the desired resistance to wear and tear and the hardness required for long-term use. Examples of suitable abrasion-resistant particles include but are not limited to mineral particles such as silica, alumina, alundum, corundum, emery, spinel, as well as other materials such as tungsten carbide, zirconium boride, titanium nitride, tantalum carbide, beryllium carbide, silicon carbide, aluminum boride, boron carbide, diamond dust, and mixtures thereof.

The overlays according to the present invention can be used for manufacture of decorative laminates, furniture components, flooring laminates and other surfaces where wear protection is needed.

In another aspect, the present invention also relates to a process for the manufacture of overlays and decorative layers and laminates according to the invention.

The decorative layer and the protective overlay according to the present invention, are prepared according to a process comprising the step of providing a fiber web layer, treating said fiber web layer with a composition comprising photocatalytic particles, a binder and optionally at least one solvent, and hardening said treated fiber web to obtain a decorative layer or a protective overlay comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.

Suitable photocatalyst particles used in the composition have been described above and are selected from the group comprising TiO_2 , ZnO , SiO_3 , $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, SrTiO_3 , Fe_2O_3 , CdS , CdSe , WO_3 , FeTiO_3 , GaP , GaAs , GeAs , RuO_2 , MoS_3 , LaRhO_3 , CdFeO_3 , Bi_2O_3 , MoS_2 , In_2O_3 , CdO , SnO_2 , SiC , InP and/or mixture thereof. In a preferred embodiment TiO_2 is used on a nanoscale size. Although not limiting, when the composition comprises a suspension in a solvent, the photocatalyst may be employed in an amount ranging from 0.01 to 5 % by weight, for example in an amount ranging from 0.01 to 1% by weight and for example in an amount ranging from 0.05 to 0.3 %.

Examples of suitable binder have been described above and include but are not limited to melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and

+3292802345

8

mixtures thereof. Although not limiting, when the composition comprises a suspension in a solvent, the binder may be employed in an amount ranging from 0.01 to 5 % by weight, for example in an amount ranging from 0.01 to 1% by weight and for example in an amount ranging from 0.05 to 0.3 %.

- 5 In a preferred embodiment said composition comprises a solvent. Suitable solvents can be selected from the group comprising water, ethylene glycol butyl ether, aliphatic linear, branched or cyclic or mixed aromatic-aliphatic alcohols having 4 to 20 carbon atoms, such as methanol, ethanol, butanol, 2-propanol, isobutanol, isopropanol, benzyl alcohol, methoxypropanol or furfuryl alcohol; and the like, and/or mixture thereof. In an
- 10 embodiment, said solvent is selected from the group comprising water, ethylene glycol butyl ether, ethanol and the like, and/or mixture thereof. In a preferred embodiment said solvent is water. The composition may further comprise additional solvent such as for example ethylene glycol butyl ether. In a preferred embodiment, said composition is a suspension comprising the photocatalyst particles, a binder and at least one solvent.
- 15 Although not limiting, the solvent can be employed individually or as a mixture, and in particular in a amount ranging from 50 to 99 % by weight, for example in an amount ranging from 80 to 99% by weight and for example in an amount ranging from 90 to 99 %.

In another embodiment, the photocatalyst particles can be dispersed or otherwise introduced into a molten, uncrosslinked, uncured or dissolved form of a suitable binder.

- 20 The composition for use in the present invention may further comprise antimicrobial agents. Although not limiting, up to 1 % by weight of antimicrobial agents may be added to the composition.

- Antimicrobial agents suitable for said composition may be any chemical capable of preventing the growth of or killing microorganisms. Examples of suitable antimicrobial
- 25 agents include, but are not limited to, quaternary ammonium, phenolic, amide, acid, and nitro compounds, and mixtures thereof. Examples of suitable quaternary ammonium compounds include, but are not limited to, 2-(3-anilinovinylul)3,4-dimethyl-oxazolinium iodide, alkylisoquinolium bromide, benzalkonium chloride, benzethonium chloride, cetylpyridinium chloride, chlorhexidine gluconate, chlorhexidine hydrochloride, lauryl
- 30 trimethyl ammonium compounds, methylbenzethonium chloride, stearyltrimethyl ammonium chloride, and mixtures thereof. Examples of suitable phenolic compounds include, but are not limited to, benzyl alcohol, p-chlorophenol, chlorocresol, chloroxylenol, cresol, o-cymene-ol (BIOSOL), hexachlorophene, hinokitiol, isopropylmethylphenol, parabens (having methyl, ethyl, propyl, butyl, isobutyl, isopropyl, and/or sodium methyl

+3292802345

9

substituents), phenethyl alcohol, phenol, phenoxyethanol, o-phnylphenol, resorcin, resorcin monoacetate, sodium parabens, sodium phenolsulfonate, thioxolone, 2,4,4'-trichloro hydroxylidiphenyl ether, zinc phenolsulfonate, di-tert.-butyl phenole, hydrochinone, and mixtures thereof. Examples of suitable amides include, but are not limited to, 5 diazolidinyl. urea, 2,4-imidazolidinedione (HYDATOIN), 3,4,4'-trichlorocarbanilide, 3-trifluoromethyl-4,41-dichlorocarbanilide, undecylenic acid monoethanolamide, and mixtures thereof, more preferably still 2,4-imidazolidinedione. Examples of suitable acids include, but are not limited to, ascorbic acid, benzoate, benzoic acid, citric acid, dehydroacetic acid, potassium sorbate, salicylic acid derivatives such as acetyl salicylic 10 acid, salicylic acid aldehyde, sodium citrate, sodium dehydroacetate, sodium salicylate, sodium salicylic acid, sorbic acid, undecylenic acid, zinc undecylenate, and mixtures thereof. Examples of suitable nitro compounds include, but are not limited to, 2-bromo nitro-2,3-propanediol (BRONOPOL), and methylidibromo glutaronitrile and propylene glycol (MERGUARD), and mixtures thereof. In a preferred embodiment said antimicrobial 15 agent is hinokitiol.

The composition according to the present invention may further comprise abrasion-resistant particles. Examples of suitable abrasion-resistant particles include but are not limited to mineral particle such as silica, alumina, alundun, corundum, emery, spinel, as well as other materials such as tungsten carbide, zirconium boride, titanium nitride, 20 tantalum carbide, beryllium carbide, silicon carbide, aluminum boride, boron carbide, diamond dust, and mixtures thereof. Considering cost availability, hardness, particle size availability and lack of color, aluminum oxide is the preferred particles.

The composition according to the present invention may also contain auxiliaries or additives such as absorbents, rheological modifiers, plasticizers, antifoaming agents, 25 antifouling agents, thixotropic agents, pigments, fillers, aggregates, extenders, reinforcing agents, flow control agents, catalysts, pigment pastes, mineral oils, wetting agents, adhesion promoters, thickening agents, flame-retarding agents, antioxidants, elastomers, antisepting agents, diluents, UV light stabilizers, air release agents, solvents, dispersing aids, and mixtures thereof, additional hardeners and additional curable compounds, 30 depending on the application.

Said treating step (b) is an impregnating step. In another embodiment said treating step (b) is selected from the group comprising dipping, flooding, coil coating, spraying, centrifuging, screen printing, vacuum infiltrating and the like.

+3292802345

10

The next step in the process according to the invention consists of the curing also referred as drying step (c).

The treated layer according to the invention is solidified, cured or otherwise hardened and processed to produce the overlay or decorative layer according to the invention. The term
5 "cured" or "dried" as used herein is not limited to materials which are cross-linked, but is open to materials which set, harden or solidify by any known means such as polymerization, heating, removal of solvent, freezing, chemical reaction, etc. The treated layer may be a decorative layer or an overlay.

10 In an embodiment said drying step may be performed by thermal hardening such as by heating, by infra red treatment, using laser and the like. Said heating may be performed for example using a metal plate, or a traditional oven and the like. Said drying step may also be performed using radiation hardening such as UV, VIS, laser hardening, electron beam hardening and the like. When the drying step is a heating step the temperature may range from room temperature to 350 °C.

15 In accordance with the present invention, the composition for use herein is applied, coated or impregnated to the surface of a fibrous sheet using a suitable coating device. The composition according to the invention can be applied to the sheet by any process used for applying a coating. Non-limiting examples of devices for depositing the composition according to the invention particles include a secondary headbox or a slot orifice coating
20 head applicator. The term "slot orifice coater" as used herein is used in the same manner it is used in the art, namely, to designate a coater having a central cavity which opens on and feeds a slot through which the coating is forced under pressure.

25 Except for the overlays and decorative layers according to the invention, the laminate of the present invention is suitably made according to standard practice and suitably has a conventional construction. The laminate is formed by superposing the different layers. The final laminate is made in the typical way such as by stacking the different layers on a suitable press or pressing plate die and subjecting the assembly to sufficient heat and pressure between the bottom pressing plate die and a highly polished upper pressing plate die for a time sufficient to produce the desired decorative laminate. The conditions of
30 pressing for both high pressure laminate and low-pressure laminate are standard and well known.

Preferably, the laminates are realized according to the classical technique which is applied for forming DPL (Direct Pressure Laminate). It is evident that, according to a

+3292802345

11

variant, the overlay and the decorative layer, already before their application on the base layer, may consist of a single layer.

The invention is intended for so-called laminated floors, but generally it can also be applied for other kinds of floor covering, comprising hard floor panels, such as veneer parquet, prefabricated parquet, or other floor panels which can be compared to laminated floor. The invention is also suitable for carpets, mats such as car mats, and the like.

After pressing, the laminate according to the present invention can be cut into individual panels. The laminates can be cut into floor panels of suitable sizes. These floor panels can be of various shape, for example, rectangular or square, or of any other shape. In an embodiment, they can be manufactured in an elongated form, with a length of for example 1 to 2 meters. The thickness can also vary. Although non-limiting, said thickness may range from 0.1 mm to 45 mm. Non limiting examples of suitable thickness range from 0.1 mm to 3 mm, from 5 to 15 mm, for example 8 mm. The panels can be provided on their side with suitable tongue and groove coupling. The groove and tongue profile is milled along the edges of the support, thereby allowing the individual panels to be joined up during the laying process. The dimensions of the profiles are designed so that adjacent panels can be pushed or hit into each other.

The laminates or panels according to the invention can be treated at their sides with a surface densifying agent, more particularly a surface hardening agent, which preferably is chosen from the following series of products: impregnation agents, pore-sealing agents, lacquers, resins, oils, paraffines and similar. This treatment can be performed over the complete surface of the sides or only over well-defined portions thereof, for example, exclusively the surfaces of the tongue and groove. The treatment with a surface densifying agent offers, in combination with the snap-together effect of the tongue and groove, the advantage that in various aspects better coupling features, are obtained. As a result of this, the coupling parts better keep their shape and strength, even if the floor panels are engaged and disassembled repeatedly.

The floor laminates or panels according to the present invention can be applied in various ways. They can be attached at the underlying floor, either by gluing or by nailing them on. According to another possibility, the floor laminates may be installed loosely onto the underground, whereby the floor laminates may mutually match into each other by means of a tongue and groove coupling, whereby mostly they are glued together in the tongue and groove, too. The floor obtained in this manner, also called a floating parquet flooring, has as an advantage that it is easy to install and that the complete floor surface can move

+3292802345

12

which often is convenient in order to receive possible expansion and shrinkage phenomena. The floor laminates may also be provided at the edges of two opposite sides, with coupling parts, co-operating with each other, substantially in the form of a tongue and a groove, whereby the coupling parts are provided with integrated mechanical locking means made in one piece with the panels which prevent the drifting apart of two coupled floor panels. The floor covering preferably is formed by joining the floor laminates into each other free of glue. Hereby, the connections are of such nature that the floor panels can be disassembled without being damaged, such that, for example, when moving, they can be taken along in order to be placed again. It is, however, clear that gluing between tongue and groove is not excluded.

The present invention provides laminates, and protective or decorative layer having photocatalytic functions such as deodorant, antimicrobial activities and the like,

The present invention is in no way limited to the forms of embodiment described herein, on the contrary may such floor laminates, overlay and decorative layer, as well as said process, be realized in different variants without leaving the scope of the invention.

+3292802345

13

Claims

1. Laminate comprising a decorative upper layer, optionally a protective overlay and optionally a base layer, wherein said decorative upper layer comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.
2. Laminate comprising a decorative upper layer, a protective overlay and optionally a base layer, wherein said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.
3. Laminate according to claim 1 or 2, wherein said fibers are cellulose fibers.
4. Laminate according to any of claims 1 to 3, wherein said photocatalyst particles are selected from the group comprising TiO_2 , ZnO , SiO_3 , $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, SrTiO_3 , Fe_2O_3 , CdS , CdSe , WO_3 , FeTiO_3 , GaP , GaAs , GeAs , RuO_2 , MoS_3 , LaRhO_3 , CdFeO_3 , Bi_2O_3 , MoS_2 , In_2O_3 , CdO , SnO_2 , SiC , InP and/or mixture thereof.
5. Laminate according to claim 4, wherein said photocatalyst particles are TiO_2 particles.
6. Laminate according to claim 4, wherein said TiO_2 particles are anatase TiO_2 particles.
7. Laminate according to any of claims 1 to 6, wherein said photocatalyst particles are doped with elements selected from the group comprising Nb, Mo, Cr, V, Cu, Mg, Ag, Ru, Au, N, Nd, Pd, Pt, Fe, Ni, Mn and the like.
8. Laminate according to any of claims 1 to 7, wherein said binder is selected from the group comprising melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof.
9. Laminate according to any of claims 1 to 8, wherein said the base layer is selected from the group comprising of fiber board, particle board, a plastic sheet and the like.
10. Laminate according to any of claims 1 to 9, further comprising at the bottom of the base layer a balancing sheet.
11. Decorative layer for laminate comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.
12. Decorative layer according to claim 11, wherein said fibers are cellulose fibers.

+3292802345

14

13. Decorative layer according to claims 11 or 12, wherein said photocatalyst particles are selected from the group comprising TiO_2 , ZnO , SiO_3 ; $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, SrTiO_3 , Fe_2O_3 , CdS , CdSe , WO_3 , FeTiO_3 , GaP , GaAs , GeAs , RuO_2 , MoS_3 , LaRhO_3 , CdFeO_3 , Bi_2O_3 , MoS_2 , In_2O_3 , CdO , SnO_2 , SiC , InP and/or mixture thereof.
- 5 14. Decorative layer according to claim 13, wherein said photocatalyst particles are TiO_2 particles.
15. Decorative layer according to claim 14, wherein said TiO_2 particles are anatase TiO_2 particles.
- 10 16. Decorative layer according to any of claims 11 to 15, wherein said photocatalyst particles are doped with elements selected from the group comprising Nb, Mo, Cr, V, Cu, Mg, Ag, Ru, Au, N, Nd, Pd, Pt, Fe, Ni, Mn and the like.
- 15 17. Decorative layer according to any of claims 11 to 16, wherein said binder is selected from the group comprising melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof.
18. Protective overlay, wherein said protective overlay comprises a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.
- 20 19. Protective overlay according to claim 18, wherein said fibers are cellulose fibers.
20. Protective overlay according to claims 18 or 19, wherein said photocatalyst particles are selected from the group comprising TiO_2 , ZnO , SiO_3 ; $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$, SrTiO_3 , Fe_2O_3 , CdS , CdSe , WO_3 , FeTiO_3 , GaP , GaAs , GeAs , RuO_2 , MoS_3 , LaRhO_3 , CdFeO_3 , Bi_2O_3 , MoS_2 , In_2O_3 , CdO , SnO_2 , SiC , InP and/or mixture thereof.
- 25 21. Protective overlay according to claim 20, wherein said photocatalyst particles are TiO_2 particles.
22. Protective overlay according to claim 21, wherein said TiO_2 particles are anatase TiO_2 particles.
- 30 23. Protective overlay according to any of claims 18 to 22, wherein said photocatalyst particles are doped with elements selected from the group comprising Nb, Mo, Cr, V, Cu, Mg, Ag, Ru, Au, N, Nd, Pd, Pt, Fe, Ni, Mn and the like.

+3292802345

15

24. Protective overlay according to any of claims 18 to 23, wherein said binder is selected from the group comprising melamine resin, urethane resin, celluloid, chitin, starch sheet, polyvinyl alcohol, polyester resins, urea-formaldehyde, dicyandiamide-formaldehyde, epoxy resins, polyurethane resins, (poly)silane resins, (poly)siloxane resins, silazane resins, acrylamides resins, acrylic silicon resins, acrylurethane resins, polyacrylamide resins and the like and mixtures thereof. .
25. Process for the production of a decorative layer or a protective overlay according to any of claims 11 to 24, comprising the step of
- a) providing a fiber web layer
 - b) treating said fiber web layer with a composition comprising photocatalyst particles, a binder and a solvent, and
 - c) hardening said treated fiber web to obtain a decorative layer or a protective overlay comprising a web of fibers having deposited therein and/or thereon photocatalyst particles embedded in a binder.
26. Process according to claim 25, wherein said solvent is selected from the group comprising water, ethylene glycol butyl ether, ethanol and the like, and/or mixture thereof.
27. Process according to claim 25 or 26, wherein said treating step (b) is an impregnating step.
28. Process according to claim 25 or 26, wherein said treating step (b) is selected from the group comprising dipping, flooding, coil coating, spraying, centrifuging, screen printing, vacuum infiltrating and the like.
29. Process according to any of claims 25 to 28 wherein said drying step (c) comprises thermal hardening, radiation hardening and the like.

+3292802345

16

Abstract

The present invention relates to laminates. More in particular it relates to laminates comprising a decorative upper layer, optionally a protective overlay and optionally a base layer, wherein said decorative upper layer comprises a web of fibers having deposited
5 therein and/or thereon photocatalyst particles embedded in a binder.

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

BRANTS, Johan, Philippe, Emile
De Clercq Brants & Partners
E. Gevaertdreef 10a
B-9830 Sint-Martens-Latem
BELGIQUE

Date of mailing (day/month/year) 06 April 2005 (06.04.2005)	
Applicant's or agent's file reference DOMO-003-PCT	IMPORTANT NOTIFICATION
International application No. PCT/EP05/000354	International filing date (day/month/year) 14 January 2005 (14.01.2005)
International publication date (day/month/year)	Priority date (day/month/year) 16 January 2004 (16.01.2004)
Applicant DOMO OUDENAARDE NV et al	

- By means of this Form, which replaces any previously issued notification concerning submission or transmittal of priority documents, the applicant is hereby notified of the date of receipt by the International Bureau of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to a date of receipt, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- (If applicable)* The letters "NR" appearing in the right-hand column denote a priority document which, on the date of mailing of this Form, had not yet been received by the International Bureau under Rule 17.1(a) or (b). Where, under Rule 17.1(a), the priority document must be submitted by the applicant to the receiving Office or the International Bureau, but the applicant fails to submit the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- (If applicable)* An asterisk (*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b) (the priority document was received after the time limit prescribed in Rule 17.1(a) or the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b)). Even though the priority document was not furnished in compliance with Rule 17.1(a) or (b), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
16 January 2004 (16.01.2004)	04447013.6	EP	24 March 2005 (24.03.2005)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Authorized officer

Brahmi Khemais

Facsimile No. +41 22 740 14 35

Facsimile No. +41 22 338 89 70
Telephone No. +41 22 338 9715